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Fax: 510.587-6090	Pages: 18 pages to follow cover sheet
Phone:	Date: December 8, 2003
Re: Disclosure and Record of Invention Form	Fax: X2611 Phone: 893.7881
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Linda-

Per the request of Sherylle Mills Englander, Director Sponsored Projects, she would prefer that Oren Liven review this disclosure. This invention disclosure is from Guillermo Bazan, Alan Heeger, Parameswar Iyer, Bin Liu, Wanli Ma, Xiong Gong and Daniel Moses titled "Water/Methanol Soluble Conjugated Copolymer as an Electron-Transport Layer in Polymer Light Emitting Diodes." I'll be mailing the original today.

☺

Tish

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b. Short descriptive title of the invention.

Water/Methanol Soluble Conjugated Copolymer as an Electron-Transport Layer in Polymer Light Emitting Diodes

2. A. Briefly summarize the invention here. Include the novel features and advantages.

A method is provided for the design of conjugated polymers suitable for improving the efficiency of polymer light emitting diodes. Water solubility provides for these materials to be spin cast on top of standard organic solvent-soluble conjugated polymers with minimum disruption of the underlying layer. There may be two components to this invention. First, general design guidelines for polymers that are soluble in polar solvents and that may serve as either an electron- or a hole-transport layer. Second, the use of these polymers in a range of organic optoelectronic devices.

B. Detailed description of the invention using additional sheets as necessary and attach as appendix.

See attached document.

3. List the funding source(s) for the project under which this invention was made. If applicable, identify by contract or grant number and name the Principal Investigator/Supervisor of each.

Funding Source/Sponsor	Contract or Grant Number	Principal Investigator/Supervisor
DuPont Displays	SB030014	Guillermo C. Bazan
UC-SMART	01-10110	Guillermo C. Bazan
Mitsubishi Chemical Corporation	Contract number SB010061	Alan J. Heeger

4. For any inventor named (item 13) who is not employed full-time by the University of California, please identify other employers (e.g., Veterans Administration, Howard Hughes Medical Institute, USDA), the percent of salary time funded by such other employer, and the nature of the other employment (such as research, teaching or clinical duties).

5. When did you first conceive this invention?

~~Information is in [redacted] (Iyer's notebook # 2, located in Bazan Group's lab/office. Chemistry 2614)~~

6. What is the date of the first written record (notebook, letter, proposal, drawing, etc.) of this invention? Identify the document, page numbers involved, and location of the document.

Information is in [redacted] (Iyer's notebook # 2, located in Bazan Group's lab/office. Chemistry 2614)

6. When did you first successfully test this invention?

The polymer was successfully synthesized on [redacted]
Devices were first tested on [redacted]

8. If you have disclosed this invention to non-UC personnel (including research sponsor) then indicate when, under what circumstances, and to whom.

a. [redacted]

b. [redacted]

c. [redacted]

c. by actual use, demonstration, or posters

7. Have you submitted or do you plan to submit a report, abstract, paper or thesis relating to this invention for publication, for presentation at a conference, or to a research sponsor?

Yes, we have prepared a manuscript, which we would like to submit to Advanced Materials as soon as possible.

If yes, give details, including the actual or planned date of submission. If a manuscript has been accepted, give the anticipated publication date. Append a copy of the latest draft manuscript available. (See instructions for the effect of publication prior to the filing of a patent application.)

8. Identify any references, patent applications, or other publications of which you are aware and which you believe to be pertinent to this invention. Please attach a copy of each of these references, if available.

See attached document.

11. If any proprietary material (e.g., cell line, antibody, plasmid, computer software, or chemical compound) obtained from outside your laboratory was used to develop this invention under a restrictive written or oral transfer agreement (other than a normal purchasing agreement), please attach a copy or summary of that agreement.

12. List companies you believe might be interested in using, developing or marketing this invention.

Mitsubishi Chemical, DuPont Displays

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14. Technically Qualified Witnesses (Two Required) - invention disclosed to and understood by:

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Dr. Hadjer Benmansour

b) [Signature] 12-5-03
Signature _____ Date _____

Print Name David A Banach
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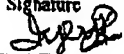
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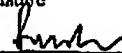
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**Water/Methanol Soluble Conjugated Copolymer as an Electron-Transport Layer
in Polymer Light Emitting Diodes**

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Abstract

*We report the synthesis of a cationic conjugated co-polymer, poly([9,9-bis(6'-
(N,N,N-trimethylammonium)hexylidene)-fluorene-2,7-diyl]-alt-[2,5-bis(p-
phenylene)-1,3,4-oxadiazole]), (polyI), and the introduction of polyI, as an electron-
transport layer (ETL) in polymer light emitting diodes (PLEDs). Multilayer PLEDs
are fabricated using semiconducting polymers cast from solution in an organic
solvent as an emissive layer and the water-soluble (or methanol-soluble) polyI, as an
ETL in the device configuration: ITO/PEDOT/emissive polymers/ETL/Ba/Al. The
results demonstrate that devices with polyI have significantly lower turn-on voltages,
higher brightness and improved luminous efficiency.*

Keywords:

Water-soluble conjugated co-polymer, electron-transporting layer, multi-layer
polymeric light-emitting diodes, electroluminescence.

The principal criteria for a polymer based electron transport layer (ETL) for use in polymer light-emitting diodes (PLEDs) are the following: (1) the lowest unoccupied molecular orbital (LUMO) of the ETL must be at an energy close to, or even within the π^* -band of the emissive semiconducting polymer; and (2) the solvent used for casting the electron injection material must not dissolve the underlying emissive polymer. Although a few attempts to satisfy these criteria have been reported, [1, 2] none has succeeded in avoiding interfacial mixing in multi-layer PLEDs.

In this contribution, we report the synthesis of the cationic conjugated alternating copolymer, poly {[9,9-bis(6'-(N,N,N-trimethylammonium)hexyliodide)-fluorene-2,7-diyl]-alt-[2,5-bis(p-phenylene)-1,3,4-oxadiazole]}, (poly1), comprising fluorene and phenylene-oxadiazole-phenylene alternating along the main chain, by the palladium catalyzed Suzuki coupling reaction (Scheme 1). Multi-layer PLEDs are fabricated using a semiconducting polymer (red, green or blue emitting) (Scheme 2), cast from solution in an organic solvent, as an emissive layer and the water-soluble (or methanol-soluble) poly1 as an ETL in the device configuration: ITO/PEDOT/emissive polymers/ETL/Ba/Al. To our knowledge, there are no previous reports of the fabrication of multi-layer PLEDs using a water-soluble conjugated polymer as an ETL to solve the interfacial mixing problem. The results demonstrate that devices with the ETL have significantly lower turn-on voltages, higher brightness and improved luminous efficiencies.

<Scheme 1>

<Scheme 2>

The synthesis of poly1 is shown in Scheme 1. Monomers 2^[2] (0.440 gm, 0.654 mmol) and 3^[4] (0.247 gm, 0.654 mmol) were dissolved in 20 mL toluene. Sodium carbonate (0.694 gm, 6.54 mmol) and Pd(PPh₃)₄ (0.037 gm, 0.0327 mmol) were

added to the reaction mixture, followed by 5 mL water. The reaction was degassed and refluxed for 48 hours under an argon atmosphere. Isolation, followed by triple precipitation into acetone gave poly{[9,9-bis(6'-(N,N-dimethylamino)hexyl)-fluorene-2,7-diyl]-alt-[2,5-bis(p-phenylene)-1,3,4-oxadiazole]} (poly4, 0.231 gm, 55 %). Addition of MeI to a solution of poly4 results in the formation of a precipitate. Addition of water renders the reaction mixture homogenous. After 48 hours poly1 can be isolated and purified by repeated precipitation into acetone in approximately 86 % yield.

Figure 1 compares the current density vs. voltage and brightness vs. voltage characteristics of devices made using PFO with and without poly1. The PFO/ETL devices turn on at ~ 3 V (the turn-on voltage is defined as the voltage at a brightness of 0.1 cd/m^2), whereas the turn-on voltage is at ~ 5 V for the PFO devices without the ETL. ^[5] At 6 V, the luminance (L) obtained from the PFO/ETL devices is $L = 3450 \text{ cd/m}^2$, compared to $L = 30 \text{ cd/m}^2$ for devices without the ETL. Similar improvements were observed from devices made with green and red emitting conjugated polymers. For MEH-PPV/ETL devices, $L = 5600 \text{ cd/m}^2$ at 5 V, compared to $L = 3550 \text{ cd/m}^2$ for similar devices fabricated without the ETL. Therefore, the addition of the ETL results in lower turn-on voltage and higher brightness. The dramatic improvement in brightness and the reduced turn-on voltage result from improved electron injection (there is a good match of the LUMO of the ETL to the π^* -band of the emissive polymer) and from the hole blocking capability of the ETL (LUMO energy at -6.24 eV relative to the vacuum).

<Figure 1>

PLEDs, the device efficiency is reduced by cathode quenching since the recombination zone is typically located near the cathode. ^[6] The addition of the ETL

moves the recombination zone away from the cathode and thereby eliminates cathode quenching. In addition, the ETL serves to block the diffusion of metal atoms, such as barium and calcium, and thereby prevents the generation of quenching centers ^[6] during the cathode deposition process. The luminous efficiency (LE in cd/A) vs. current density (J in mA/cm²) for devices with and without the ETL are shown in Figure 2a, 2b and 2c. As shown in Figure 2, devices with ETL have higher luminous efficiency, higher power efficiency, and correspondingly higher brightness at a given voltage.

<Figure 2>

The improvements in LE and PE can be understood in greater detail by comparing the LUMO energy levels of the emissive polymers with that of poly1 and the work-function of barium (see Scheme 3). The energy barrier between the LUMO of PFO and the work function of barium is ~ 0.6 eV. Thus, by adding the poly1 layer, electron injection is enhanced. For PFO-BT and MEH-PPV, there is no energy barrier for electron injection. However, the hole-blocking feature of poly1 leads to better balanced electron and hole currents. In addition, the enhanced electron injection can also facilitate hole injection. ^[7] Therefore, the larger and more nearly balanced electron and hole currents lead to higher luminous efficiencies in the devices with the ETL.

<Scheme 3>

Interfacial energetics are known to play an important role in the emission characteristics of organic LEDs. ^[8, 9] By adding the ETL between the cathode and the emissive polymer, the contacts at both interfaces are improved. Atomic force microscope (AFM) images show that the surface roughness of the ETL is larger than that of the emissive polymer. As a result, more effective electron injection is achieved

simply because of the increased contact area between ETL and cathode.

In conclusion, the water-soluble (and methanol soluble) conjugated co-polymer poly1, was designed, synthesized and then introduced as the ETL in multi-layer PLEDs. By casting the ETL from solution in methanol and the emissive layer from an organic solvent solution, interfacial mixing is avoided. Using blue, green or red emitting semiconducting polymers as the emissive layer and poly1 as the ETL, significant improvements in performance have been demonstrated. More importantly, our results indicate that high-performance multi-layer PLEDs can be fabricated by processing all the layers from solution.

Experimental

Characterization of polymer 3: ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.29 (m, 4H), 7.87 (m, 6H), 7.68 (m, 4H), 2.14 (m, 20H), 1.30 (m, 4H), 1.13 (m, 8H), 0.77 (m, 4H). ^{13}C NMR (125MHz, CDCl_3 , ppm): δ 164.76, 152.07, 144.97, 140.91, 139.12, 127.95, 127.62, 126.54, 121.60, 120.67, 59.91, 55.64, 45.57, 40.57, 30.11, 27.70, 27.31, 24.05. Gel permeation chromatography (GPC) analysis shows a molecular weight of $M_n = 19300$ g/mol and a polydispersity of 1.04.

Characterization of polymer 4: ^1H NMR (400 MHz, DMSO, ppm): δ 8.30 (m, 4H), 8.07 (m, 6H), 7.88 (m, 4H), 3.13 (m, 4H), 2.94 (m, 22H), 1.43 (m, 4H), 1.06 (m, 8H), 0.61 (m, 4H). ^{13}C NMR (125MHz, DMSO, ppm): δ 168.94, 151.58, 149.42, 143.62, 137.91, 127.65, 127.62, 126.58, 122.15, 120.98, 65.13, 55.28, 52.05, 42.94, 30.74, 28.710, 25.38, 21.88.

Poly(9,9-dihexyl-fluorene-co-benzothiadiazole) (PFO-BT) was synthesized using the Suzuki coupling reaction.^[10, 11] Poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) and poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) were

purchased from American Dye Source, Inc. (Canada). The molecular structures of PFO, PFO-BT, and MEH-PPV are shown in Scheme 2. The HOMO (highest occupied molecular orbital) and LUMO energy levels of PFO, PFO-BT, MEH-PPV and poly1 are shown in Scheme 3. The work functions of poly(3,4-ethylene dioxythiophene): poly(styrene sulfonic acid) (PEDOT:PSS) and barium are also shown for comparison in Scheme 3.

For device fabrication, we utilized PEDOT:PSS on indium tin oxide (ITO) as the hole-injecting bilayer electrode. PLEDs were fabricated with and without the ETL layer in the following device structures: (ITO)/PEDOT:PSS/Emissive polymer/Ba/Al and (ITO)/PEDOT:PSS/Emissive Polymer/ETL/Ba/Al. Details of device fabrication and testing have been reported elsewhere; all fabrication steps were carried out inside a controlled atmosphere dry box under nitrogen atmosphere.^[12, 13] The ETL was deposited on top of the emissive layer by spin-casting from solution in methanol (0.6% wt.-%) to form a poly1 layer with thickness of approximately 30 nm and then annealed at 90°C for 2 hours to remove residual solvent. Hydrophilic methanol was used as the solvent (rather than water) to achieve better inter-layer wetting while maintaining well-defined multi-layers. Throughout this report, we will use the term "emissive polymer/ETL" to designate devices with the ETL.

Acknowledgement

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Figures and Schemes captions:

Scheme 1. Synthesis of poly1 and poly4.

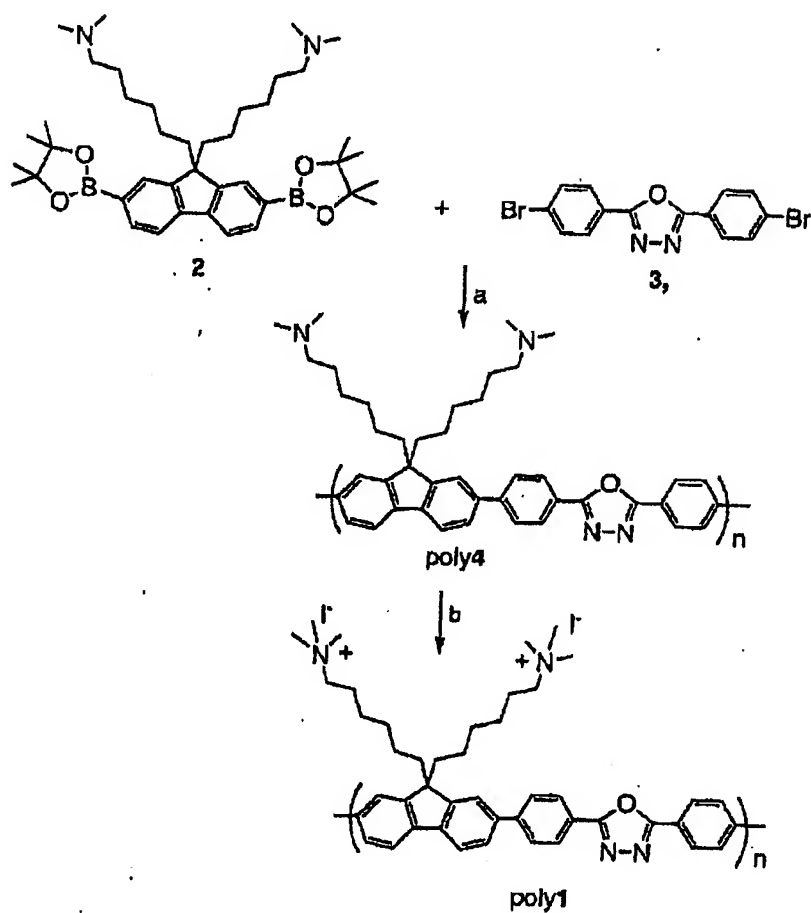
Scheme 2. Molecular structures of PFO, PFO-BT, and MEH-PPV.

Scheme 3. The HOMO and LUMO energy levels of PFO, PFO-BT, MEH-PPV and poly1 compared to the work function of Ba (all referenced with respect to the vacuum).

Figure 1. The current density (mA/cm^2) vs. applied voltage (V) and luminance (cd/m^2) vs. applied voltage (V) for devices made using blue-emitting PFO with and without the ETL.

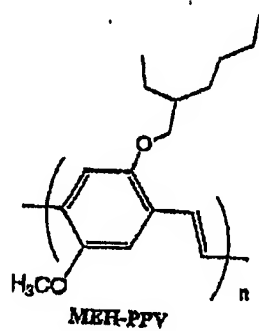
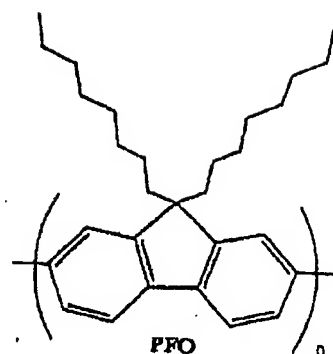
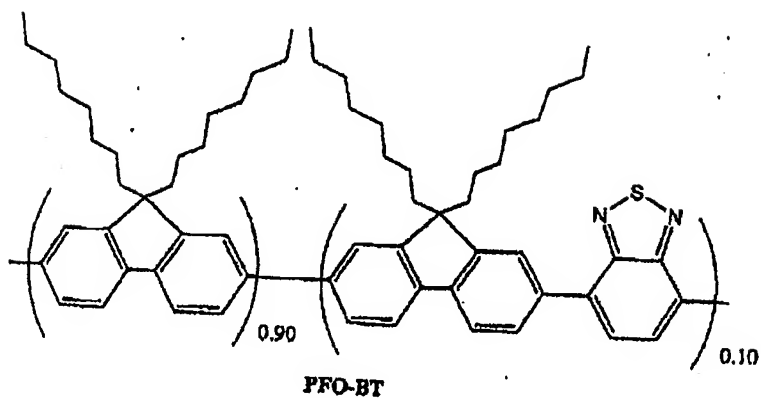
Figure 2. The luminous efficiency (cd/A) as a function of current density (mA/cm^2) for devices made with (a) PFO, (b) PFO-BT and (c) MEH-PPV with and without ETL. Insets: (a) Power efficiency (lm/W) vs. bias (V) for devices made by PFO with and without ETL; (b) and (c) brightness (cd/m^2) vs. current density (mA/cm^2) for devices made by PFO-BT and MEH-PPV with and without poly1.

Scheme 1. Synthesis of poly1 and poly4.

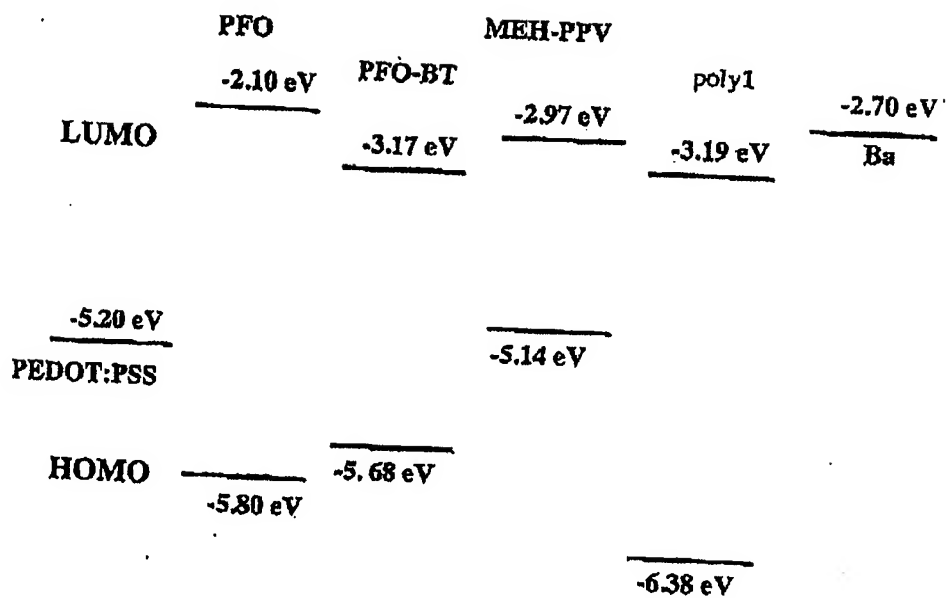


a = Toluene, water, Pd(PPh₃)₄, Na₂CO₃, 120 deg/48 hrs
b = THF, water, Iodomethane, RT/48 hrs

Scheme 2. Molecular Structures



Scheme 3. Energy Levels



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Figure 1

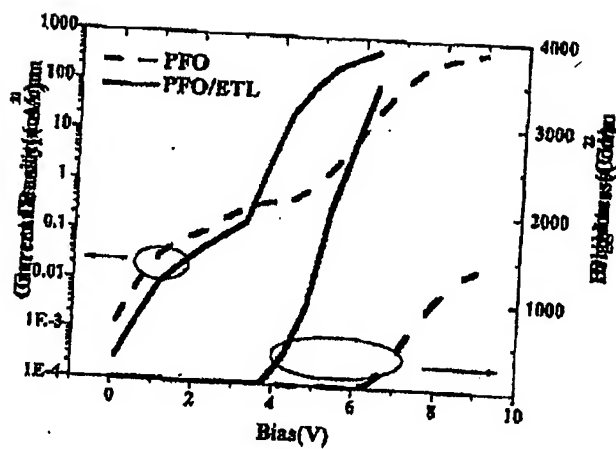


Figure 2

